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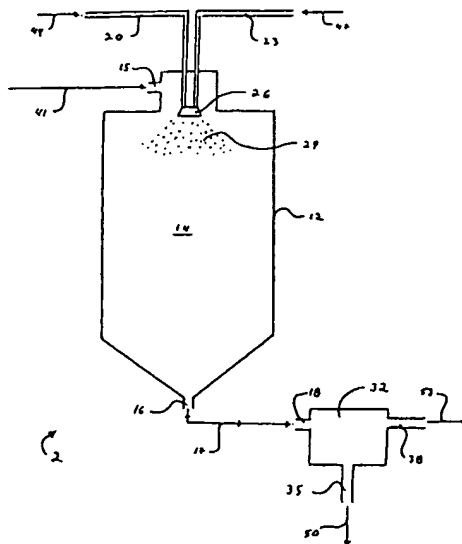
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(54) Title: METHOD OF PREPARING ANHYDROUS ALKALI METAL SULFIDES



(57) Abstract: Anhydrous alkali metal sulfide is prepared by (a) atomizing an aqueous composition comprising water and alkali metal sulfide (e.g., sodium hydrosulfide, sodium monosulfide and sodium tetrasulfide); (b) contacting the atomized aqueous composition with a first inert gas stream to form a second inert gas stream containing solid particulate anhydrous alkali metal sulfide; and (c) separating the solid particulate anhydrous alkali metal sulfide from the second inert gas stream. The atomized aqueous composition may be contacted with the first inert gas stream at substantially atmospheric pressure in a spray dryer.

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## METHOD OF PREPARING ANHYDROUS ALKALI METAL SULFIDES

## DESCRIPTION OF THE INVENTION

The present invention relates to a method of preparing  
5 anhydrous alkali metal sulfide, e.g., sodium tetrasulfide  
( $\text{Na}_2\text{S}_4$ ). More particularly, the present invention relates to a  
method of preparing anhydrous alkali metal sulfide, which  
includes the steps of atomizing an aqueous composition  
comprising water and alkali metal sulfide, contacting the  
10 atomized aqueous composition with a first inert gas stream to  
form a second inert gas stream containing solid particulate  
anhydrous alkali metal sulfide, and separating solid  
particulate anhydrous alkali metal sulfide from the second  
inert gas stream.

15 Alkali metal sulfides are useful as chemical reagents in,  
for example, dye production and polymer synthesis. Alkali  
metal sulfides are typically available in the form of aqueous  
solutions or solid hydrated flakes or pearls. Commercially  
available alkali metal sulfides in solid hydrated flake form  
20 generally contain between 30 and 40 percent by weight of  
water, based on total weight. The water that is present in  
the solid hydrated alkali metal sulfide may interfere with  
chemical reactions in which it is used, e.g., decreasing rates  
of reaction and/or process yields. Accordingly, the use of  
25 anhydrous alkali metal sulfides would be preferred for certain  
chemical reactions and processes. Anhydrous sodium  
monosulfide ( $\text{Na}_2\text{S}$ ) and/or anhydrous sodium hydrosulfide ( $\text{NaHS}$ ),  
for example, can be used advantageously in the synthesis of  
poly(phenylene sulfide).

30 United States Patent No. 1,946,089 describes the  
preparation of anhydrous sodium monosulfide ( $\text{Na}_2\text{S}$ ) by heating  
hydrous sodium monosulfide, e.g.,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , under reduced  
pressure in a kettle. The crystal mass that forms within the  
kettle is described in the '089 patent as having an almost  
35 dough-like consistency, which must be plowed and turned over

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with a plow-type agitator throughout the vacuum heating process.

United States Patent No. 2,533,163 describes the preparation of anhydrous sodium monosulfide ( $\text{Na}_2\text{S}$ ) from solid  
5 hydrated sodium monosulfide, e.g.,  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ . The solid hydrated sodium monosulfide is heated under reduced pressure to 750-850°C at such a rate that no fusion of the sodium monosulfide occurs.

United States Patent No.'s 5,071,632 and 5,173,088  
10 describe the two-stage preparation of crystals of anhydrous sodium monosulfide. In the first stage, a solid polyhydrate of sodium monosulfide is heated under a pressure of 500 Torr or less, and in the second stage further heating is performed under atmospheric pressure or reduced pressure. European  
15 Patent Application No. 924,165 A1 describes the preparation of anhydrous sodium monosulfide by heating solid water-containing sodium monosulfide in a contact drier under a pressure of less than 20 Torr.

N.I. Kopylov, in The  $\text{Na}_2\text{S}\text{-H}_2\text{O}$  System and the Thermal  
20 Dehydration of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , *Russian Journal of Inorganic Chemistry* 1968, 13(2), pp 276-278, describes the preparation of pure anhydrous sodium monosulfide from  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  by direct, low-temperature drying at a pressure of 30-35 mm of mercury (Hg). Kopylov also describes the dehydration of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  by  
25 heating in a stream of hydrogen, with remelting of the product; and the dehydration of a hydrate of sodium monosulfide in a carbon tube, which was slowly heated in a Kryptol furnace and held at 350-400°C in a stream of purified nitrogen.

30 United States Patent No. 4,908,043 describes the preparation of single crystals of anhydrous sodium monosulfide. The '043 patent describes concentrating an aqueous solution of sodium monosulfide, at a temperature of at least 97°C, from which single crystals of anhydrous sodium  
35 monosulfide are precipitated.

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The spray drying of sodium monosulfide ( $\text{Na}_2\text{S}$ ) in a 5.5 meter (18 foot) diameter by 5.5 meter high spray dryer using heated air is described in *Chemical Engineers' Handbook*, Fifth Edition, Robert H. Perry, Cecil H. Chilton, Sidney D.

- 5 Kirkpatrick; McGraw-Hill, Inc; New York, 1973; Chapter 20, page 60, Table 20-32. However, it is known that sodium monosulfide, and in particular anhydrous sodium monosulfide, undergoes autoxidation when exposed to air, and forms polysulfur, thiosulfate and sulfate (e.g., as described by
- 10 David R. Bush; Sodium Sulfides, *Kirk-Othmer Encyclopedia of Chemical Technology*, Fourth Edition; Jacqueline Kroschwitz, Mary Howe-Grant; John Wiley & Sons; New York, 1997; Volume 22, pp 411-419. See in particular page 415).

- It is desirable to pursue the continued development of
- 15 new methods of preparing anhydrous alkali metal sulfides. It is further desirable that such newly developed methods not result in the formation of fused or oxidized products, and not require the use of reduced pressure.

- In accordance with the present invention, there is
- 20 provided a method of preparing anhydrous alkali metal sulfide comprising:

(a) atomizing an aqueous composition comprising water and alkali metal sulfide;

- (b) contacting said atomized aqueous composition
- 25 with a first inert gas stream to form a second inert gas stream containing solid particulate anhydrous alkali metal sulfide; and

(c) separating solid particulate anhydrous alkali metal sulfide from said second inert gas stream.

- 30 The features that characterize the present invention are pointed out with particularity in the claims, which are annexed to and form a part of this disclosure. These and other features of the invention, its operating advantages and the specific objects obtained by its use will be more fully
- 35 understood from the following detailed description and the

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accompanying drawing in which an embodiment of the invention is illustrated and described.

Other than in the operating examples, or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions, etc, used in the specification and claims are to be understood as modified in all instances by the term "about."

#### BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a schematic representation of spray dryer means used to prepare anhydrous alkali metal sulfides according to the method of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

In accordance with the method of the present invention, an aqueous composition comprising water and alkali metal sulfide is atomized in a manner that minimizes oxidation of the sulfide and produces an anhydrous product. To minimize oxidation of the alkali metal sulfide, the aqueous stream is preferably atomized in an inert atmosphere. As used herein and in the claims by "inert atmosphere" and similar terms, e.g., "inert gas" and "inert gas stream," is meant an inert atmosphere, gas or gas stream that is substantially free of oxygen, i.e., containing oxygen in an amount less than 0.1 percent by volume, and preferably less than 0.05 percent by volume, based on total volume. The inert gas of the inert atmosphere in which the aqueous composition is atomized may be selected from nitrogen, helium, argon and mixtures thereof. Preferably, the inert gas of the inert atmosphere is nitrogen. The inert atmosphere is generally provided by the first inert gas stream.

The aqueous composition is typically atomized by passing it through an atomizer. Atomizers that may be used in the present invention include those known to the skilled artisan, for example, spray nozzles and disk or bell atomizers. The operation of a disk atomizer generally involves continuously

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applying a stream of the aqueous composition to the surface of a rapidly spinning disk. Disk atomizers useful in the present invention may optionally be operated with an atomizing inert gas stream to further enhance the atomization of the aqueous composition and/or shape and direct the atomized aqueous composition coming off of the disk.

In an embodiment of the present invention, the aqueous composition is atomized by means of a spray nozzle into which the aqueous composition is fed either alone or in combination with an atomizing inert gas stream. The aqueous composition is typically fed into the spray nozzle under pressure, e.g., at a pressure of at least 670 kilopascals (100 pounds per square inch). When used, the atomizing inert gas stream is also fed into the spray nozzle under pressure, typically at a pressure equal to that under which the aqueous composition is fed. The inert gas of the atomizing inert gas stream may be selected from nitrogen, helium, argon and mixtures thereof. Preferably, the inert gas of the atomizing inert gas stream is nitrogen.

The aqueous composition typically contains alkali metal sulfide in an amount of at least 20 percent by weight, preferably at least 30 percent by weight and more preferably 40 percent by weight, based on the total weight of the aqueous composition. The aqueous composition also typically contains alkali metal sulfide in an amount less than 70 percent by weight, and preferably less than 65 percent by weight, based on the total weight of the aqueous composition. The amount of alkali metal sulfide present in the aqueous composition may range between any combination of these values, inclusive of the recited values. While aqueous compositions containing more than 70 percent by weight of alkali metal sulfide may be used in the present invention, they generally are not easily atomized, e.g., they are more likely to clog a spray nozzle atomizer. While the scope of the present invention is also inclusive of aqueous compositions containing less than 20 percent by weight of alkali metal sulfide, their use is

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generally inefficient, e.g., the amount of energy (and therefore the cost) required to drive off more than 80 percent by weight of water from the aqueous composition can be excessively large and uneconomical.

5       The aqueous composition comprising alkali metal sulfide may also contain small amounts (e.g., up to 10 percent by weight, based on total weight) of other materials that are typically coproducts of the method by which the alkali metal sulfide was prepared. Examples of other materials that may be  
10 present in the aqueous composition include, but are not limited to, alkali metal hydroxide, alkali metal thiosulfate, alkali metal carbonate and iron. For example, an aqueous composition containing 60 percent by weight of sodium monosulfide, also typically contains either 0.8 percent by  
15 weight of sodium hydrosulfide or 0.4 percent by weight of sodium hydroxide, 0.7 percent by weight of sodium thiosulfate, 0.3 percent by weight of carbon dioxide in the form of sodium carbonate, and 8 parts per million parts (ppm) of iron, all percent weights being based on the total weight of the aqueous  
20 composition. The remainder of the aqueous composition is alkali metal sulfide and water.

The aqueous composition may be in the form of a suspension, dispersion, solution or a combination thereof. To optimize atomization of the aqueous composition, it is  
25 preferable that it be in the form of a solution. Depending on the amount and type of alkali metal sulfide present in the aqueous composition, the aqueous composition may be frozen or solid at ambient room temperature, which requires that it be heated prior to atomization.

30       Prior to atomization, the temperature of the aqueous composition comprising alkali metal sulfide is preferably greater than the freezing point and less than the boiling point of the aqueous composition. Both the freezing and the boiling points of the aqueous composition will depend on the  
35 amount and type of alkali metal sulfide present in the aqueous composition. For example, aqueous solutions containing

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different concentrations of sodium hydrosulfide (NaHS) have the following freezing point (F.Pt.) and boiling point (B.Pt.) values: 25 percent by weight NaHS, F.Pt. =  $-23^{\circ}\text{C}$ , B.Pt. =  $110^{\circ}\text{C}$ ; 45 percent by weight NaHS, F.Pt. =  $14^{\circ}\text{C}$ , B.Pt. =  $127^{\circ}\text{C}$ ; 5 and 60 percent by weight NaHS, F.Pt. =  $40^{\circ}\text{C}$ , B.Pt. =  $143^{\circ}\text{C}$ . For purposes of further illustration, aqueous solutions containing different concentrations of sodium monosulfide ( $\text{Na}_2\text{S}$ ) have the following freezing point and boiling point values: 10 percent by weight  $\text{Na}_2\text{S}$ , F.Pt. =  $-10^{\circ}\text{C}$ , B.Pt. =  $103^{\circ}\text{C}$ ; 30 percent by weight  $\text{Na}_2\text{S}$ , F.Pt. =  $59^{\circ}\text{C}$ , B.Pt. =  $121^{\circ}\text{C}$ ; 10 and 60 percent by weight  $\text{Na}_2\text{S}$ , F.Pt. =  $92^{\circ}\text{C}$ , B.Pt. =  $173^{\circ}\text{C}$ .

The alkali metal of the alkali metal sulfide may be selected from lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs) and mixtures thereof (in which case 15 the alkali metal sulfide is a mixed alkali metal sulfide). Preferably the alkali metal of the alkali metal sulfide is selected from sodium, potassium and mixtures thereof. Examples of alkali metal sulfides that may comprise the aqueous composition include, but are not limited to, alkali 20 metal hydrosulfides, alkali metal monosulfides, alkali metal polysulfides containing at least 2 sulfur atoms (e.g., from 2 to 11 sulfur atoms), and mixtures thereof.

In an embodiment of the present invention, the alkali metal sulfide is selected from alkali metal hydrosulfide, 25 alkali metal monosulfide, alkali metal disulfide, alkali metal trisulfide, alkali metal tetrasulfide, alkali metal pentasulfide and mixtures thereof. Specific examples of alkali metal sulfides that may comprise the aqueous composition and that may be formed into anhydrous alkali metal 30 sulfides in the present invention, include but are not limited to, sodium hydrosulfide (NaHS), potassium hydrosulfide (KHS), lithium monosulfide ( $\text{Li}_2\text{S}$ ), sodium monosulfide ( $\text{Na}_2\text{S}$ ), potassium monosulfide ( $\text{K}_2\text{S}$ ), potassium sodium monosulfide (NaKS), lithium disulfide ( $\text{Li}_2\text{S}_2$ ), sodium disulfide ( $\text{Na}_2\text{S}_2$ ), 35 potassium disulfide ( $\text{K}_2\text{S}_2$ ), rubidium disulfide ( $\text{Rb}_2\text{S}_2$ ), cesium disulfide ( $\text{Cs}_2\text{S}_2$ ), sodium trisulfide ( $\text{Na}_2\text{S}_3$ ), potassium



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trisulfide ( $K_2S_3$ ), cesium trisulfide ( $Cs_2S_3$ ), sodium tetrasulfide ( $Na_2S_4$ ), potassium tetrasulfide ( $K_2S_4$ ), sodium pentasulfide ( $Na_2S_5$ ), potassium pentasulfide ( $K_2S_5$ ), rubidium pentasulfide ( $Rb_2S_5$ ), sodium hexasulfide ( $Na_2S_6$ ), cesium  
5 hexasulfide ( $Cs_2S_6$ ), sodium heptasulfide ( $Na_2S_7$ ), sodium octasulfide ( $Na_2S_8$ ), sodium nonasulfide ( $Na_2S_9$ ), sodium decasulfide ( $Na_2S_{10}$ ) and sodium undecasulfide ( $Na_2S_{11}$ ).

The atomized aqueous composition comprising alkali metal sulfide is contacted with a first inert gas stream, and a  
10 second inert gas stream containing solid particulate anhydrous alkali metal sulfide is formed. The inert gas of the first inert gas stream may be selected from nitrogen, helium, argon and mixtures thereof. Typically, the inert gas of the first inert gas stream is nitrogen. The first inert gas stream is  
15 preferably substantially free of water, e.g., having a dew point of  $-40^\circ C$ .

In the method of the present invention, the atomized aqueous composition is typically contacted with the first inert gas stream at pressures of from 740 Torr to 800 Torr,  
20 e.g., at substantially atmospheric pressure. More often, the atomized aqueous composition is contacted with the first inert gas stream at a pressure equal to or slightly greater than atmospheric pressure, e.g., from 760 Torr to 800 Torr.

The first inert gas stream is typically heated prior to  
25 contacting the atomized aqueous composition. The temperature of the first inert gas stream is selected such that it will be at least sufficient to dehydrate the atomized aqueous composition with which it is contacted and form the second inert gas stream containing solid particulate anhydrous alkali  
30 metal sulfide before the hydrated alkali metal sulfide reaches the outlet of the chamber in which atomization is conducted. The temperature of the first inert gas stream is also selected such that melting of the anhydrous alkali metal sulfide is minimized. If the temperature of the first inert gas stream  
35 is too high, the particulate anhydrous alkali metal sulfide that is formed may melt to a degree that molten or partially

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molten particles collide and form larger particles or agglomerates that fall out of the second inert gas stream prior to collection.

The temperature to which the first inert gas stream is heated is typically at least 100°C, preferably at least 250°C, and more preferably at least 275°C. The temperature of the first inert gas stream is also typically less than 1000°C, preferably less than 800°C, and more preferably less than 500°C. The temperature of the first inert gas stream may range between any combination of these values, inclusive of the recited values. The first inert gas stream may be heated by means known to the skilled artisan, e.g., by passing the first inert gas stream over the heating coils of an electrically powered heat exchanger.

In an embodiment of the present invention, the aqueous composition comprises from 20 percent by weight to 70 percent by weight, based on the total weight of the aqueous composition, of an alkali metal sulfide selected from the group consisting of sodium hydrosulfide, sodium monosulfide, sodium disulfide, sodium tetrasulfide and mixtures thereof. The temperature of the aqueous composition is from 90°C to 120°C, and the first inert gas stream is heated to a temperature of from 275°C to 500°C.

The second inert gas stream contains (a) the inert gas of the first inert gas stream, (b) solid particulate anhydrous alkali metal sulfide, and (c) water which is typically in the form of vapor or gas. The solid particulate anhydrous alkali metal sulfide is separated from the second inert gas stream. Typically, the solid particulate anhydrous alkali metal sulfide is separated from the inert gas and water vapor of the second inert gas stream by means of a gas-solid separator, such as a cyclone separator. The gas-solid separator means separates the second inert gas stream into: (i) solid particulate anhydrous alkali metal sulfide, which may be collected; and (ii) a third inert gas stream containing the inert gas and water vapor of the second inert gas stream. The

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third inert gas stream may be either vented into the atmosphere (if it contains no environmentally objectionable materials) or forwarded for further processing.

The separated solid particulate anhydrous alkali metal sulfide may be transferred for immediate use in a chemical reaction, or more typically is stored in suitable containers, e.g., sealed 50 gallon steel drums, under a dry inert atmosphere, e.g., under dry nitrogen. The solid particulate anhydrous alkali metal sulfide separated in the method of the present invention, is typically free-flowing or pourable and may have a wide range of particle sizes, e.g., having the free-flowing particulate consistency of commercially available talcum body powders or table sugar. The particle size of the particulate anhydrous alkali metal sulfide will depend in part on the design and type of atomizer used. Solid particulate anhydrous alkali metal sulfide prepared in accordance with the method of the present invention is substantially free of water, e.g., containing less than 500 ppm or less than 300 ppm of water.

The third inert gas stream resulting from the separation of solid particulate anhydrous alkali metal sulfide from the second inert gas stream may optionally be further processed and recycled in the method of the present invention. For example, the water vapor in the third inert gas stream may be removed by known means of dehydration to form a fourth inert gas stream. The fourth inert gas stream may then be recycled and contacted with the atomized aqueous composition alone or in combination with the first inert gas stream.

The method of the present invention may be performed in what is commonly referred to as a spray dryer. Spray dryers generally comprise a housing having a chamber therein (sometimes referred to as a drying chamber), and at least one inlet and at least one outlet, each providing gaseous communication with the chamber. Spray dryers also typically include at least one atomizer, from which atomized liquids are propelled into the chamber. The operation of a spray dryer

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generally involves introducing a gas stream into the chamber by way of the inlet, introducing an atomized liquid into the chamber by means of the atomizer, allowing the introduced gas stream and the atomized liquid to contact each other within  
5 the chamber, and removing a gas stream containing a solid particulate material through the outlet of the chamber. The atomized liquid and gas stream introduced into the chamber of the spray dryer may contact each other in a cocurrent, countercurrent or mixed flow mode, depending on the design of  
10 the spray dryer, as is known to the skilled artisan.

In Figure 1 there is represented schematically a spray dryer that is useful in performing the method of the present invention. The spray dryer 2 of Figure 1 comprises a housing 12 having a chamber 14 therein, an inlet 15, and an outlet 16.  
15 Inlet 15 and outlet 16 are each in gaseous communication with chamber 14. Spray dryer 2 also includes an atomizer 26, which is a spray nozzle. Atomizer 26 is located within chamber 14, and occupies a position that is closer to inlet 15 than to outlet 16. Atomizer 26 has an atomizing inert gas stream  
20 inlet 20 and an aqueous composition inlet 23.

A first inert gas stream is introduced into chamber 14 through inlet 15 by means of a suitable conduit represented by line 41. The first inert gas stream is heated prior to introduction into chamber 14 by first passing it through at  
25 least one heat exchanger, not shown. An atomizing inert gas stream is introduced under pressure into inlet 20 of atomizer 26 by means of a suitable conduit represented by line 44, and an aqueous composition comprising water and alkali metal sulfide is introduced under pressure into inlet 23 of atomizer  
30 26 by means of a suitable conduit represented by line 47. The inert atomizing gas stream and the aqueous composition mix within atomizer 26, and an atomized aqueous composition 29 is propelled from the atomizer into chamber 14.

Within chamber 14, the atomized aqueous composition 29 is  
35 contacted with the first inert gas stream in a cocurrent fashion at substantially atmospheric pressure, and forms a

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second inert gas stream containing solid particulate anhydrous alkali metal sulfide (not shown), the inert gas of the first inert gas stream and water vapor. The second inert gas stream is removed from chamber 14 through outlet 16, and is forwarded  
5 to gas-solid separator means 32 by a conduit represented by line 17. The second inert gas stream is introduced into separator 32 through inlet 18. Solid particulate anhydrous alkali metal sulfide is removed from gas-solid separator 32 through outlet 35, and is forwarded through a conduit  
10 represented by line 50 for collection in a suitable container (not shown).

A third inert gas stream containing the inert gas and water vapor of the second inert gas stream is removed from separator 32 through outlet 38 and forwarded through a conduit  
15 represented by line 53. The third inert gas stream forwarded through conduit 53 may be vented to the atmosphere (if it does not contain any environmentally objectionable materials). In an embodiment of the present invention, the third inert gas stream is forwarded through conduit 53 for further processing,  
20 e.g., removal of water and reheating, and is then reintroduced into chamber 14 through inlet 15 by means of conduits and valves not shown.

The operation of a spray dryer as represented in Figure 1 can be optimized by controlling or selecting the rates,  
25 temperatures and compositions (e.g., the concentration of alkali metal sulfide in the aqueous composition) of the feed streams going into the spray dryer. By optimized operation is meant that a maximum amount of solid particulate alkali metal sulfide is removed from the spray dryer with a minimum  
30 expenditure of energy (e.g., the energy required to heat the first inert gas stream) and raw materials (e.g., the amount of first inert gas stream introduced into the spray dryer). Such an optimal balance of operating conditions is typically arrived at by trial and error, and depends in part on the  
35 dimensions of the spray dryer.

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The present invention is more particularly described in the following embodiments, which are intended to be illustrative only, since numerous modifications and variations therein will be apparent to those skilled in the art.

5 In an embodiment of the present invention, solid particulate anhydrous sodium hydrosulfide is prepared in a vertically mounted spray dryer similar to that represented in Figure 1. The spray dryer can be fabricated from stainless steel, have an inner diameter of 91 centimeters, and a length  
10 of 4.5 meters (3.5 meters cylindrical and 1 meter conical).

The operation of the spray dryer during the preparation of solid particulate anhydrous sodium hydrosulfide can be described generally with reference to Figure 1. Heated nitrogen gas is introduced into chamber 14 of spray dryer 2  
15 through inlet 15 at a temperature of for example 418°C and at a rate of 3.7 cubic meters per minute. The nitrogen gas fed into inlet 15 can be heated by first passing it through electrically powered heat exchangers (not shown). Chamber 14 is maintained at substantially atmospheric pressure throughout  
20 the operation of the spray dryer. The spray dryer is typically operated continuously over a period of, for example, at least 3 to 6 hours.

An aqueous composition comprising 60 percent by weight sodium hydrosulfide, based on the total weight of the aqueous  
25 composition, is fed at a temperature of 110°C, a pressure of 7 kilograms per square centimeter ( $\text{Kg/cm}^2$ ) and at a rate of 10 to 11 kilograms per hour through inlet 23 into atomizer 26 (e.g., the 1/4 JBC SS nozzle from Spray Systems Co.). Atomizing nitrogen is concurrently fed through inlet 20 into atomizer 26  
30 at a pressure of 7  $\text{Kg/cm}^2$  and at a rate of 4.8 liters per minute. The aqueous composition emerges from atomizer 26 and is introduced in an atomized form into chamber 14 where it comes into contact with the heated nitrogen gas introduced through inlet 15. An inert gas stream containing solid  
35 particulate anhydrous sodium hydrosulfide is removed from the spray dryer through outlet 16 at a temperature of 200°C, and

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forwarded through conduit 17 to cyclone separator 32. Solid particulate anhydrous sodium hydrosulfide product is separated from the inert gas stream in separator 32, collected and stored in steel drums under dry nitrogen gas.

5        In another embodiment of the present invention, solid particulate anhydrous sodium monosulfide is prepared from an aqueous composition comprising 30 percent by weight sodium monosulfide, based on the total weight of the aqueous composition, in a spray dryer similar to that represented in  
10 Figure 1 and as previously described with regards to the preparation of anhydrous sodium hydrosulfide. Heated nitrogen gas, the aqueous sodium monosulfide composition, and atomizing nitrogen gas are each fed into spray dryer 2 at the same temperatures, pressures and rates as described previously for  
15 the preparation of anhydrous sodium hydrosulfide. An inert gas stream containing solid particulate anhydrous sodium monosulfide is removed from the spray dryer through outlet 16 at a temperature of 200°C, and forwarded through conduit 17 to cyclone separator 32. Solid particulate anhydrous sodium  
20 monosulfide product is separated from the inert gas stream in separator 32, collected and stored in steel drums under dry nitrogen gas.

      In yet another embodiment of the present invention, solid particulate anhydrous sodium disulfide is prepared from an  
25 aqueous composition comprising 45 percent by weight sodium disulfide, based on the total weight of the aqueous composition, in a spray dryer similar to that represented in Figure 1 and as previously described with regards to the preparation of anhydrous sodium hydrosulfide. Heated nitrogen  
30 gas, the aqueous sodium disulfide composition, and atomizing nitrogen gas are each fed into spray dryer 2 at the same temperatures, pressures and rates as described previously for the preparation of anhydrous sodium hydrosulfide. An inert gas stream containing solid particulate anhydrous sodium  
35 disulfide is removed from the spray dryer through outlet 16 at a temperature of 200°C, and forwarded through conduit 17 to

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cyclone separator 32. Solid particulate anhydrous sodium disulfide product is separated from the inert gas stream in separator 32, collected and stored in steel drums under dry nitrogen gas.

5 In a still further embodiment of the present invention, solid particulate anhydrous sodium tetrasulfide is prepared from an aqueous composition comprising 60 percent by weight sodium tetrasulfide, based on the total weight of the aqueous composition, in a spray dryer similar to that represented in  
10 Figure 1 and as previously described with regards to the preparation of anhydrous sodium hydrosulfide. Heated nitrogen gas and atomizing nitrogen gas are each fed into spray dryer 2 at the same temperatures, pressures and rates as described previously for the preparation of anhydrous sodium  
15 hydrosulfide. The aqueous sodium tetrasulfide composition is fed through inlet 23 into atomizer 26 at a rate of 26 kilograms per hour. An inert gas stream containing solid particulate anhydrous sodium tetrasulfide is removed from the spray dryer through outlet 16 at a temperature of 170°C, and  
20 forwarded through conduit 17 to cyclone separator 32. Solid particulate anhydrous sodium tetrasulfide product is separated from the inert gas stream in separator 32, collected and stored in steel drums under dry nitrogen gas.

In the described embodiments of the present invention,  
25 each of the aqueous compositions (i.e., the aqueous compositions comprising sodium hydrosulfide, sodium monosulfide, sodium disulfide or sodium tetrasulfide) may also contain from 0.2 to 2 percent by weight of sodium thiosulfate, from 0.1 to 0.3 percent by weight of carbon dioxide in the  
30 form of sodium carbonate, and from 2 to 5 ppm of iron, all percent weights being based on the total weight of the aqueous compositions. Anhydrous sodium hydrosulfide, sodium monosulfide and sodium disulfide, prepared in accordance with the described embodiments of the present invention, each have  
35 a free flowing particulate consistency approximating that of commercially available talcum body powder. Anhydrous sodium



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tetrasulfide prepared in accordance with the described embodiment of the present invention, has a free flowing particulate consistency approximating that of table sugar.

The present invention has been described with reference  
5 to specific details of particular embodiments thereof. It is not intended that such details be regarded as limitations upon the scope of the invention except insofar as and to the extent that they are included in the accompanying claims.

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We claim:

1. A method of preparing anhydrous alkali metal sulfide comprising:
  - (a) atomizing an aqueous composition comprising  
5 water and alkali metal sulfide;
  - (b) contacting said atomized aqueous composition with a first inert gas stream to form a second inert gas stream containing solid particulate anhydrous alkali metal sulfide; and  
10 (c) separating solid particulate anhydrous alkali metal sulfide from said second inert gas stream.
2. The method of claim 1 wherein said alkali metal sulfide is selected from the group consisting of alkali metal  
15 hydrosulfide, alkali metal monosulfide, alkali metal disulfide, alkali metal trisulfide, alkali metal tetrasulfide, alkali metal pentasulfide and mixtures thereof.
3. The method of claim 1 wherein said aqueous  
20 composition contains from 20 percent by weight to 70 percent by weight of alkali metal sulfide, based on the total weight of said aqueous composition.
4. The method of claim 3 wherein the temperature of said  
25 aqueous composition is greater than the freezing point and less than the boiling point of said aqueous composition.
5. The method of claim 4 wherein said aqueous composition is in the form of a solution.  
30
6. The method of claim 1 wherein said aqueous composition is atomized in an inert atmosphere.
7. The method of claim 6 wherein the inert gas of said  
35 inert atmosphere is selected from the group consisting of nitrogen, helium, argon and mixtures thereof.

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8. The method of claim 7 wherein the inert gas of said inert atmosphere is nitrogen.

5        9. The method of claim 1 wherein the inert gas of said first inert gas stream is selected from the group consisting of nitrogen, helium, argon and mixtures thereof.

10       10. The method of claim 9 wherein the inert gas of said first inert gas stream is nitrogen.

15       11. The method of claim 1 wherein said atomized aqueous composition is contacted with said first inert gas stream at substantially atmospheric pressure.

12. The method of claim 1 wherein said first inert gas stream is substantially free of water.

20       13. The method of claim 1 wherein said first inert gas stream is heated prior to contacting said atomized aqueous composition.

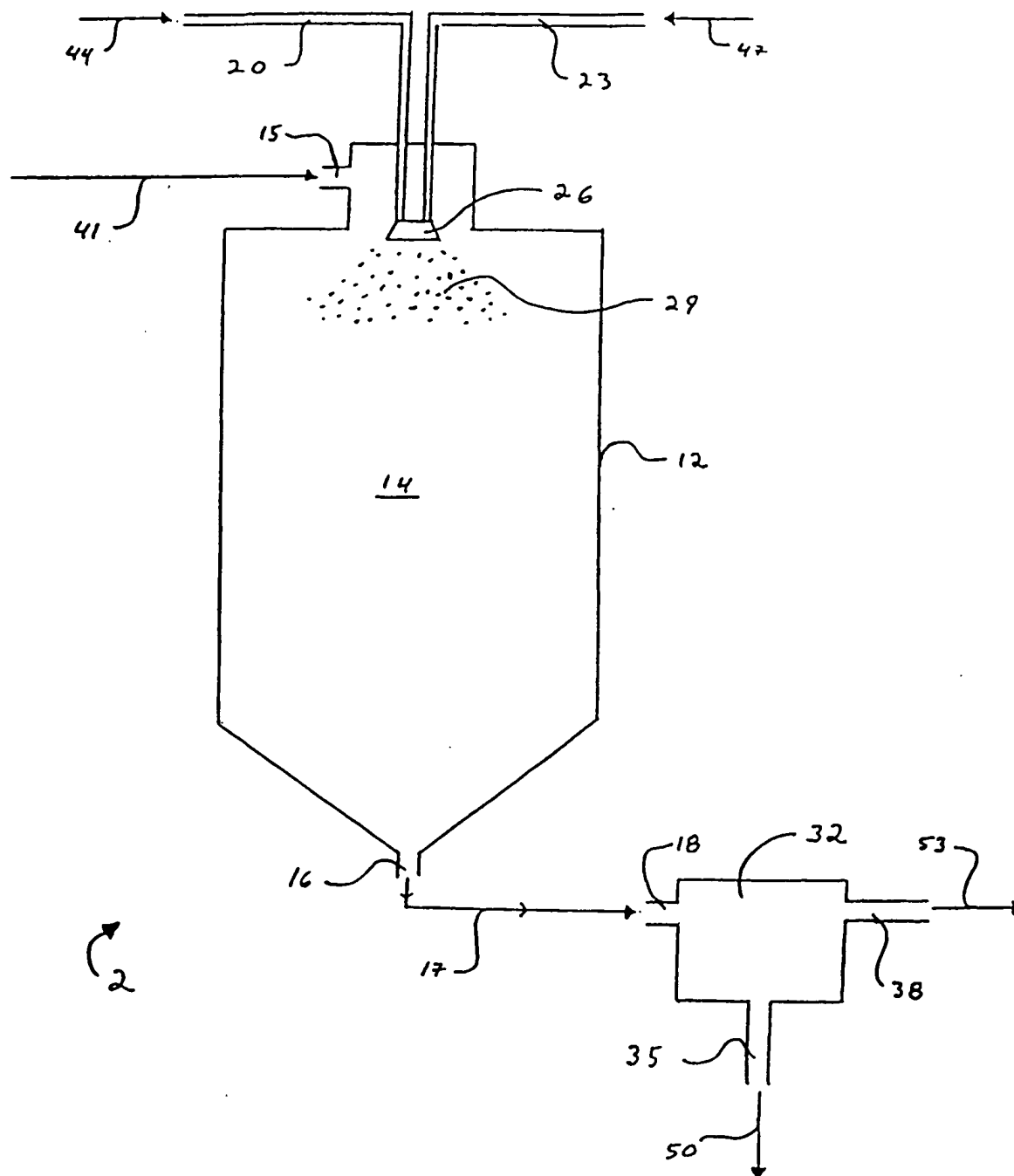
25       14. The method of claim 13 wherein said alkali metal sulfide is selected from the group consisting of sodium hydrosulfide, sodium monosulfide, sodium disulfide, sodium tetrasulfide and mixtures thereof, and said aqueous composition contains from 20 percent by weight to 70 percent by weight of said alkali metal sulfide, based on the total weight of said aqueous composition.

30       15. The method of claim 14 wherein the temperature of said aqueous composition is from 90°C to 120°C, and said inert gas is heated to a temperature of from 275°C to 500°C.

35       16. The method of claim 15 wherein the inert gas of said first inert gas stream is nitrogen.






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

Figure 1



## Method for producing anhydrous sodium sulfide

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### Abstract of EP0924165

In the production of anhydrous sodium sulfide, sodium sulfide containing 35-45% water with mixing is passed through an apparatus, in which the product temperature of approximately 20 degrees C at the place of solid injection gradually rises to at least 180 degrees C while the subpressure is maintained at less than 20, preferably less than 11 torr.